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DEPARTMENT OF CHEMISTRY

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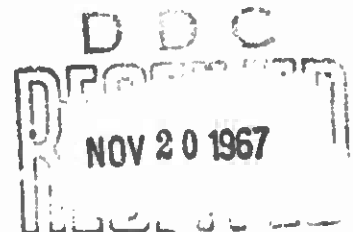
Quarterly Report No. 9

(May 1, 1967 through July 31, 1967)

"COMBUSTION CHARACTERISTICS OF CRYSTALLINE OXIDIZERS"

By: Harold C. Beachell and
E. Ellsworth Hackman

September, 1967



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the tube burning experiments; and at atmospheric pressure the burning rate in air is some 2 1/2 times that of A.P. This is quite remarkable in that it is known that when blended with A.P. in propellant, the burning rate is cut in half. However, this is just a more striking example of the importance of both A^* , the characteristic combustion surface and oxygen to fuel ratio on combustion. We are now working to get particle shapes and sizes equivalent to those that have been tested for A.P. for a direct comparison. Combustion of DNG in a nitrogen atmosphere will tell whether or not its fuel rich combustion gases (See Table I, Part VII) mix rapidly enough with ambient air to affect the burning rate of the solid.

VI. Combustion Quenching or Extinction

In studying combustion mechanisms it is important to know what conditions will cause cessation of burning. It is well known that sufficient cooling of the burning system will force it below the autoignition point, and quench combustion entirely. This has been achieved in two ways: 1) rapid adiabatic expansion, and 2) spraying with sufficient water. It has been postulated that a highly hydrated and inert solid compound in powder form could have a better chance than water of contacting the solid surface when injected into a burning system.

A candidate solid should be highly hydrated, and highly stable after loss of the bound water. A search of inorganic compounds yielded $Al_2(SO_4)_3 \cdot 18H_2O$. This compound is nearly 50% by weight water, and the resultant $Al_2(SO_4)_3$ has a highly negative heat of formation and thus contributes little to any combustion reaction.

In an attempt to get a preliminary indication of the effects of this compound, it was blended with AP -40+50 mesh powder and the resultant mixture ignited for burning in air at atmospheric pressure.

When 2% hydrated aluminum sulfate was blended with A.P., the burning rate was the same as pure A.P. However, increasing to 5% sulfate caused a drastic change in combustion conditions. The samples, though successfully ignited, would only burn a short distance before self extinguishment. This seems to indicate that at this level of addition, the endothermic effects are strong enough to counterbalance the strongly exothermic AP combustion and actually cool the system below the autoignition point.

As time permits, some consideration is also being given to highly stable organic molecules as burning modifiers.

I. Introduction

A fundamental understanding of the combustion characteristics of a range of physical conditions of crystalline oxidizers is important if complete knowledge pertaining to the combustion and stability characteristics of composite solid propellants is to be attained. This research involves theoretical and experimental studies of the burning of crystalline oxidizers ranging in physical form from large single crystals to low bulk density powders. A strandburner, window bomb and high-speed motion picture photography will be used to obtain burning rates versus pressure, and to record stability of combustion for a variety of particle sizes and pressure (density) packings of selected crystalline oxidizers (i.e., ammonium perchlorate) and analogous compounds. The study of large single crystal burning will remove particle size, shape and packing factors as complications. Data from low bulk density powder combustion studies, when compared with single crystal data, provides vital information about combustion zone thickness, ignition and conductivity contributions to the overall combustion phenomena. In addition, it is believed that simple combustion tests of powder oxidizer samples can serve as an efficient screening technique for determining whether chemical modifications have increased or decreased the intrinsic burning rate. Crystalline decomposition mechanisms observed during burning will be related to the oxidizer intrinsic burning rate and the basic properties of the oxidizer such as chemical nature, crystal type, and ion sizes. The validity of the models will be determined by correlation with the experimental data obtained.

II. Chemical Modifications - Doping

During this period several types of modifications to the basic A.P. combustion were investigated. It was found that doping of A.P. (or cocrystallization with it) by small concentrations (0.2 and 2%) of the divalent strontium cation was easily achieved when rapid crystallization methods were used which gave fine particle crystals. Powder combustion tests in air at atmospheric pressure gave the same burning rate as for pure A.P. of equivalent particle size and bulk density. This would seem to show that Sr^{++} replacement for NH_4^+ in the A.P. lattice, which would provide additional electron traps, and impede electron transfer, has not struck at a fundamental or rate limiting step in the overall combustion reaction. However, it was most interesting to find that when single crystals were grown from an A.P. solution containing 2% by weight of $\text{Sr}(\text{ClO}_4)_2$, there was no detectable level of Sr^{++} present as determined by flame photometry and electrical conductivity. The latter method is believed to be the

most sensitive to concentrations in the parts per billion range. After considering the relative solubilities of the two perchlorate compounds, it was realized that far greater concentrations of the more soluble strontium ion would be required to achieve doping. We did not want to add other less soluble strontium compounds in the higher concentrations thereby complicating the anion structure of the crystals. This work is continuing with the aim of getting strontium ion doping, at the parts per million level, of otherwise pure and perfect single A.P. crystals. If, as has been predicted, these crystals exhibit strong reduction in electrical conductivity, combustion tests will be run to determine the correlation between this mode of conductivity and combustion phenomena. Unfortunately, the measurement of the electrical conductivity of powder is far less accurate, so that we cannot relate the powder burning to any conductivity values.

III. Deuterated A.P.

ND_4ClO_4 of greater than 99% purity was prepared by triple recrystallization from D_2O , using pure A.P. as a starting material. The fine crystalline product was dried and screened to obtain a -40+50 mesh sample. This was loaded into 4 mm tubes and burned, with pure A.P. samples as controls. When bulk density was held constant, there was no difference in burning rate in air at atmospheric pressure between the two oxidizers. This would indicate that at least under these conditions, the abstraction of hydrogen from NH_4^+ was not rate limiting. If it had been, the slower rate of breaking N-D bonds, as compared with N-H bonds, would have had its effect. The comparison still must be made at higher pressures; say 68 atm.

IV. HAP-AP Comparisons

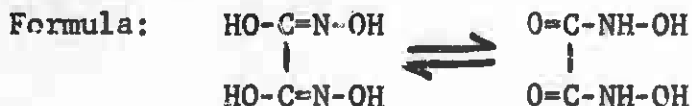
It is interesting that the replacement of one hydrogen by hydroxyl, to give $\text{NH}_3\text{OHClO}_4$, hydroxyl ammonium perchlorate (HAP), produces a profound change in melting or decomposition point and other properties. Whereas A.P. decomposes at 460°C ., HAP melts at 80°C . and then exhibits a major exotherm at 180°C ., and rapid vaporization at 228°C . HAP begins to take on water when the relative humidity at 75°F . is about 8%; whereas A.P. does not appear to do so at any r.h. Although the burning rate in equivalent propellant formulations using either oxidizer (hydrocarbon binder 15%, aluminum 15%, HAP or AP 70%) is 0.4 to 0.5 inches/second at 1000 psia, the HAP formulation is somewhat more sensitive to detonation by shock. As shown by McHale, the oxidizer powders themselves burn quite differently. HAP will not burn in glass tubes at pressures below 100 atmospheres, whereas AP will burn down to 20 atm.

One thing we would like to determine is the importance of a liquid film at the oxidizer burning surface. Since Price has found that AP has one, although extremely thin, and McHale and Von Elbe have found such layers on hydrazine perchlorate and diperchlorate, it has been postulated by Price that important reactions take place in that layer. Possibly lower pressure deflagration limits are caused by vaporization of the liquid layers before key reactions can take place.

V. New Monopropellant - Dihydroxyglyoxime (DHG)

In order to expand the scope of the reactions available for study of burning rate, some attention is being given to another monopropellant which has unique burning properties. Pure DHG has not as yet been subjected to a study of its burning properties by other laboratories, however, it is finding use as a flame temperature and burning rate suppressor when used in A.P. propellants.¹

Some properties of DHG follow:



Decomposition: melting with rapid decomposition to H_2O , CO_2 and NH_3 takes place at 170°C . (See Section VII for high temperature decomposition data)

Crystal density: 1.85 g/cc

ΔH_f : -136.3 kcal/mol.

Water solubility: 0.46 g/100 ml. H_2O at 25°C .

In combustion tests with DHG we have used the fine needle-like crystals of 10 to 50 microns that form naturally under a variety of conditions. Thin platelets are also sometimes formed. This physical form gives very low bulk densities (30-40% of crystal density) in

(1) E. S. Sutton, E. J. Pacanowsky, "Designing Propellants For Gas Generators", ICRPG/AIAA 2nd Solid Propulsion Conference Papers, June 6-8, 1967. Published by AIAA,

the tube burning experiments; and at atmospheric pressure the burning rate in air is some 2 1/2 times that of A.P. This is quite remarkable in that it is known that when blended with A.P. in propellant, the burning rate is cut in half. However, this is just a more striking example of the importance of both A*, the characteristic combustion surface and oxygen to fuel ratio on combustion. We are now working to get particle shapes and sizes equivalent to those that have been tested for A.P. for a direct comparison. Combustion of DMG in a nitrogen atmosphere will tell whether or not its fuel rich combustion gases (See Table I, Part VII) mix rapidly enough with ambient air to affect the burning rate of the solid.

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As time permits, some consideration is also being given to highly stable organic molecules as burning modifiers.

VII. A.P. Combustion Model

The most important theoretical task to be accomplished is the establishment of a model for A.P. combustion which will be in accord with the observations made in this laboratory and those recorded in the literature. We are ultimately interested in giving a step by step account of the reactions occurring as a perfect A.P. crystal lattice is subjected to an ignition source.

The following are the kinds of information we seek at a reference pressure and initial cold solid temperature in order to establish a model:

1. Thickness of the liquid melt on the crystal surface.
2. Distance from the liquid surface to the closest station in the gas at the adiabatic flame temperature.
3. Absolute time for species to traverse the distance in 2, above.
4. Density and temperature gradients in the solid and gas phases.
5. Composition of the liquid melt.
6. Gradient analyses to show the growth and decay in concentration of several key gas phase species.
7. Estimates of collision frequencies at any station in the gas phase.
8. By combining data from 6 and 7 above, and then estimating remaining species and concentrations, calculate energy release at any station.
9. Prediction of the temperature profile in the gas phase by balancing 8 above with heat absorbed from downstream station, and heat transmitted to upstream station.
10. Measured temperature profile for confirmation of 9.

For reference purposes, equilibrium compositions of adiabatic combustion species for two monopropellants were determined using a

general computer program² adapted to the IBM 7040 system. Pressures of interest were 1, 34 and 68 atmospheres (or 14.7, 500 and 1000 psia).

This computer program uses the latest available high pressure, high temperature equilibrium data for all species of importance. The calculation is easily completed once the temperature and composition of the reaction products are known at the combustion pressure. The temperature and composition data can be determined from an appropriate combination of equations describing the: 1) conservation of atomic species; 2) chemical equilibrium; 3) Dalton's law of partial pressures and 4) conservation of enthalpy or entropy.

These equations do not constitute a linear set, and are thus solved by an iterative technique. The Newton Raphson method, well suited to computer operations, is used.

(2) "A General Method for Automatic Computation of Equilibrium Compositions and Theoretical Rocket Performance of Propellants" by S. Gordon, F. J. Zeleznik and V. N. Huff; NASA Technical Note D-132 Lewis Research Center, Cleveland, Ohio, Sept. 1959.

TABLE I

Dihydroxyglyoxime Monopropellant Combustion Equilibrium Data

Heat of Formation (Enthalpy) kcal/mole -136.3 Initial Temp.
298.15° K, Density 1.85 g/cc

<u>Parameters</u>	<u>Pressure</u>		
	<u>1 atm.</u>	<u>34 atm.</u>	<u>68 atm.</u>
Temp., Degrees K	1247	1253	1264
Temp., Degrees F	1784	1795	1816
Enthalpy, cal/g	-1135.2	-1135.2	-1135.2
Entropy, cal/g-°K	2.476	2.184	2.127
Average Molecular Wt.	24.014	24.066	24.163
Heat Capacity, cal/g-°K	0.437	0.484	0.563
Ratio of Specific Heats c_p/c_v	1.234	1.225	1.213
<u>Combustion Species,</u>			
<u>Moles/100 grams</u>			
CH ₄	0.0000	0.0042	0.0123
CO	0.9225	0.9177	0.9082
CO ₂	0.7432	0.7439	0.7452
H ₂	0.7432	0.7304	0.7067
H ₂ O	0.9225	0.9260	0.9327
NH ₃	0.0000	0.0006	0.0012
N ₂	0.8328	0.8325	0.8323

Additional products which were considered but whose mole fractions were less than 0.000005 for all assigned conditions: Carbon (gas or solid), CH, CHO, CN, H, NH, OH, N, NO, O, O₂.

TABLE II

Ammonium Perchlorate Monopropellant Combustion Equilibrium Data

Heat of Formation (Enthalpy)	-70.69 kcal/mole
Initial Temperature	298.15° K
Density	1.95 g/cc

<u>Parameters</u>	<u>Pressure</u>		
	<u>1 atm.</u>	<u>34 atm.</u>	<u>68 atm.</u>
Temp., Degrees K	1375	1397	1403
Temp., Degrees F	2015	2054	2066
Enthalpy, cal/g	-601.6	-601.6	-601.6
Entropy, cal/g-°K	2.212	1.960	1.911
Average Molecular Wt.	27.691	27.871	27.930
Heat Capacity cal/g-°K	0.352	0.364	0.367
Ratio of Specific Heats c_p/c_v	1.264	1.259	1.258

Combustion Species
Moles/100 grams

Cl	0.0054	0.0022	0.0019
HCl	0.8168	0.7301	0.7005
ClO	0.0001	0.0002	0.0002
Cl ₂	0.0144	0.0593	0.0742
OH	0.0002	0.0001	0.0001
H ₂ O	1.2937	1.3371	1.3519
NO	0.0011	0.0013	0.0013
N ₂	0.4250	0.4249	0.4249
O ₂	1.0546	1.0329	1.0254

Additional products which were considered but whose mole fractions were less than 0.000005 for all assigned conditions: H, NH, H₂, NH₃, N and O.

Comparing Tables I and II, it can be seen that the A.P. combustion species are about as far on the oxygen rich side (molecular oxygen) as the DHG species are on the fuel rich side (hydrogen and carbon monoxide.) Further comparisons of the combustion response of these two dissimilar materials should give us new insight into combustion mechanisms.

VIII. Conclusions

1. Small concentrations of strontium ion replacing ammonium ion in A.P. (or $\text{Sr}(\text{ClO}_4)_2$ cocrystallized with A.P.) do not affect the powder burning rates.
2. In growing large single doped crystals, the relative solubilities must be balanced carefully by concentrations proportional to those solubilities.
3. NH_4^+ ion reaction during A.P. combustion is not rate limiting, at least at atmospheric pressure.
4. As evidenced by HAP-AP comparisons, some rather fundamental chemical changes may not affect propellant burning rate greatly.
5. DHG is a monopropellant whose combustion species are about as fuel rich as the AP combustion species are oxygen rich.
6. At the 5 weight percent level, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ causes extinction of A.P. burning at ambient pressure.

IX. Future Work

1. Growth of Sr^{++} doped single crystals.
2. Combustion of deuterated AP powder at 1000 psi.
3. Modification of DHG powder particle size for direct comparison with A.P.
4. Further investigation of chemical quenching.
5. Improvement of the single crystal combustion model.

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13. ABSTRACT Various modifications to the monopropellant solid oxidizer ammonium perchlorate are described. Cation replacement, or "doping" of AP by Sr ion and deuteration to provide ND ₄ ClO ₄ did not alter the burning rate from that of pure NH ₄ ClO ₄ at 14.7 psia. Hydrated aluminum sulfata shows an ability to extinguish AP combustion at the 5% level, whereas 2% does not even alter the burning rate at atmospheric pressure. The theoretical adiabatic combustion species for AP and dihydroxy glyoxime (DHG) at 1, 34 and 68 atmospheres are given. DHG produces fuel rich rather than oxygen rich monopropellant combustion species.			

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	ROLE	WT	ROLE	WT	ROLE	WT
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Deuterated ammonium perchlorate						
Burning Rate						
Combustion extinction						
Combustion species						